# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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## AN ELECTRON-MICROSCOPE STUDY OF USED NITRIDED-STEEL PISTON RINGS

By Thomas P. Clark and Walter A. Vierthaler

Aircraft Engine Research Laboratory
Cleveland, Ohio



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## SUMMARY

A critical study of the altered surface layers found on nitrided-steel piston rings run in nitrided-steel cylinder barrels was conducted to determine the physical and chemical characteristics of the altered layers and the mechanism by which these coating layers were formed. The electron microscope was used for the examination of areas that heretofore could be studied only by electron and X-ray diffraction. The light microscope was used to study gross microstructures and oxidation-color patterns. The following information was obtained as a result of the investigation:

1. The running faces of nitrided-steel piston rings smeared during engine operation and a metallic layer that consisted of a virtually amorphous crust with an underlayer of finely fragmented crystals was deposited on the ring face.

2. The granular portion of the coating layer had chemical properties similar to those of the underlying nitrided steel but the vitreous top layer had a high resistance toward oxidation and corrosion.

3. The smooth portion of the coating was apparently formed by a melting and flowing of the surface as a result of friction-developed temperatures; whereas, the granular portion of the coating was apparently formed by a fragmentation and subsequent smearing of the strained surface crystals as a result of elevated temperatures and high surface pressures.

## INTRODUCTION

Surface films and coatings generated on piston rings, bearings, and other rubbing parts of aircraft engines during their operation are of interest because of the decrease in wear and the increased load-carrying capacity of run-in surfaces having such coatings. Studies of these coatings are being conducted at the NACA Cleveland laboratory in an attempt to identify their composition, grain

structure, and the mechanism of their formation (references 1, 2, and 3). This information should aid in the choice of alloys best suited for rubbing parts. A determination of the method of formation is a preliminary step to a possible synthesis of pretreated surfaces having the desirable characteristics imparted by run-in.

The surface coating found on nitrided-steel piston rings (reference 1) is ideal for a general study of surface deformation and coating formation. The purpose of the investigation reported herein was to study the chemical reactivity and microstructure of the rubbing surface and its components. The corrosion resistance and the surface deformation of nitrided-steel piston rings run in nitrided-steel cylinder barrels were studied by examining segments of piston rings etched with various reagents. The electron microscope was utilized to examine the surfaces at high magnification. The microstructure of the deformed crystals was determined with the aid of stereoscopic electron micrographs. The rate of oxidation of different portions of the worn surface was determined by means of heat-tinting.

## APPARATUS

### Metallurgical (Light) Microscope

A Bausch and Lomb research-model metallograph was utilized to examine the etched and heat-tinted specimens and to take the desired light micrographs. A light-blue daylight filter was used in the examination and photography of the heat-tinted specimens.

### Electron Microscope

An RCA electron microscope, type EMB-4, was used to take the electron micrographs of the specimen replicas. These replicas were mounted in the RCA 4° stereo holder and stereoscopic pictures were made of all the regions of interest. The instrument magnification was determined by measuring electron micrographs of replicas of a ruled diffraction grating (reference 4). The original electron micrographs were made at an electronic magnification of 4000 diameters and optically enlarged to the magnification shown in the report.

### Stereoscopic Electron Micrographs

The relatively great depth of focus of the electron microscope makes possible the taking of stereoscopic pictures at high magnification. The stereo holder is so constructed that rotating the holder 180° between consecutive pictures of the same field gives a stereoscopic pair of negatives. Prints of these negatives when properly arranged and examined through a viewing device reveal the three-dimensional microstructure of the original specimen. Representative stereoscopic electron micrographs of the surfaces studied in connection with this report are included as figures 1 to 6. These figures can be examined with the Abrams aerial-mapping contour finder, model FC-2, as outlined in reference 5. Prints of only one member of each pair (figs. 7 to 19) are discussed.

## EXPERIMENTAL PROCEDURE

### Preparation of Specimens

The cross sections and the running faces of new and used nitrided-steel piston rings were studied to determine the characteristics of the surface deformation. The rings were cut into $1\frac{1}{4}$-inch segments to facilitate handling. The specimens intended for cross-sectional study were carefully cleaned and electroplated with a layer of nickel approximately 0.03 inch thick. The segments intended for a study of the running face were cleaned but were not nickel-plated. The plated segments were cut into transverse slices one-eighth inch thick and mounted in Bakelite by means of a metallographic mounting press. Some of the plated cross sections intended for light-microscope examination and heat-tinting studies were mounted in an alloy with a low melting point. These mounted specimens were carefully polished metallographically for satisfactory observation at high magnification.

### Chemical Etching of Specimens

The cross sections to be examined with the light microscope were given a 3-second etch with 2-percent nital.

The specimens intended for heat-tinting were given a 2-second etch with 2-percent nital and thoroughly dried. The low-melting-point alloy was then melted and the specimens were removed and placed face up on a brass plate heated to approximately 300° C. The

specimens were removed and cooled after the ring section had been heat-tinted to a red-purple core and a dark-blue case. The tinted specimens were then remounted in the alloy for examination under the light microscope.

The cross-section specimens from which replicas were made for the electron microscope were etched for 30 seconds with 2-percent nital.

The segment of the used ring utilized for an electron-micrographic study of the running face was first etched for 30 seconds with 2-percent nital. After satisfactory pictures were obtained, the segment was etched for 5 seconds with aqua regia. When the study of this etching treatment was finished, the segment was finally boiled for 30 minutes in concentrated potassium hydroxide. The new ring segment was given the same treatment.

## Preparation of Replicas for the Electron Microscope

Metal surfaces cannot be directly examined in the electron microscope because an electron beam can penetrate only thin films a few millionths of an inch thick. Instead, thin replicas of the ring samples were used to study the surface characteristics imparted by the various reagents. The two-step polystyrene-silica method (reference 6) is one of the best existing processes for preparing replicas to be used in the electron microscope. A modification of this method (reference 7) was utilized for preparing all the replicas of which electron micrographs appear in this report.

When the mounted cross-section specimens had been etched, they were again placed in the metallographic mounting press and enough methyl methacrylate (Lucite) molding powder was added to make a molded disk approximately 0.005 inch thick. After the mold had cooled, the mounted specimen was taken from the mold and the paper-thin disk of plastic was carefully loosened with a dissecting needle. The plastic disk was placed replica side down on a frame in a high-vacuum apparatus and after a vacuum of 0.1 micron or better was attained, a thin film of silica was evaporated on the replica disk from a small tungsten coil. This silica film was a positive replica of the original surface (reference 6).

The silicated replica was cut into 1/8-inch squares with a paper cutter. The area to be studied was kept in the center of the squares. A rim of 10-percent gelatine solution was painted on the edge of a specimen screen and when it became sticky the replica

square was pressed replica side down against the screen with the desired portion at the center of the screen. The gelatine dried within 15 minutes and the whole mount was immersed, screen down, in a flat dish containing freshly distilled chloroform. After 30 minutes the Lucite had dissolved, leaving the silica replica stuck to the screen with gelatine. The screen was removed, dried, and examined in the electron microscope.

The etched unplated segments of the ring were inserted with the running face up between the semicircular halves of a split Bakelite plug with the top rounded to conform to the radius of curvature of the piston ring. The plug was of such a thickness that the ring face of the segment formed a continuous surface with the tops of the plug halves. A Lucite disk of 1/32-inch thickness was molded on this curved surface. The Lucite replicas were cracked off and coated with a silica film as before. The silica was scraped from the disk except for the strip representing the ring face. This strip was scratched into 1/8-inch squares with a razor blade and the disk was immersed in chloroform where the silica squares floated free of the plastic in a few minutes. The squares were removed with a fine-wire mesh paddle and transferred to a second dish of chloroform for washing. The residual Lucite dissolved from the replicas within a few minutes. The silica replicas were then floated onto 1/8-inch specimen screens and mounted in the holders for electron-microscope examination.

## RESULTS

### Light Micrographs of Piston-Ring Cross Sections

Preliminary experiments reported in reference 1 indicated that the coating substance found on worn nitrided-steel piston rings possessed a smooth structureless-appearing cross section, which was not visibly attacked by the usual metallographic reagents but could be darkened by hot concentrated potassium hydroxide. Results of the examination reported herein, however, have revealed that a completely smooth coating was characteristic of areas where little crystal deformation was evident under the coating; this deformation is shown in figure 7. When the crystal deformation under the coating layer increased, the coating became thicker and began to appear granular at the junction of the coating and the underlying crystals. In extreme cases where severe crystal deformation and working had occurred, a thick layer of granular worked metal was found underneath the coating, which was occasionally completely granular as shown in

figure 8. The granular coating sometimes appeared stratified with no definite relation between the thickness of the coating and the number of layers present.

The edge of the ring face, which received a severe loading at the top of the stroke, often showed a deep pocket of deformed crystals covered with a thick lens-shaped layer of coating. In some cross sections the worked crystal layers built up at the edge of the ring and the coating jutted out over the worked crystal layer as if it had been smeared. All variations of the coating were observed on the same cross section.

In most of the cases a cross section of the ring revealed the coating to be only partly granular as shown in figure 9. The smooth top portion of the coating seemed to be formed to a limited depth of approximately 0.0001 inch. Thick layers of coating formed on severely worked surface crystals have therefore a relatively thick layer of granular coating, whereas thin layers may have only a trace of granular material at the junction of the coating and the surface crystals.

The line of demarcation between the coating and the worked crystals was usually distinct but a tongue of the underlying deformed crystals occasionally projected into the coating, which suggested that the coating transformation sometimes occurred in the surface layers of crystals without dislodging them. The top of the coating layer is usually flat but instances were observed where a waviness and extreme fluctuations of coating thickness occurred even though the underlying surface was relatively flat.

## Light Micrographs of Heat-Tinted Piston-Ring Cross Sections

The oxidation rate of metal crystals can be determined by studying the interference colors of oxide films formed on metal surfaces. When an oxide film reaches a critical thickness, the shortest visible wavelengths in the violet region of the spectrum are suppressed and the remainder of the spectrum is reflected (reference 8). This residue of light is complementary to the extinguished wavelengths, which results in a yellow reflection from the film. As the film becomes progressively thicker, the longer wavelengths are suppressed; the shorter are transmitted; and the oxide film passes through a series of colors complementary to the absorbed colors (wavelengths). Table I lists the colors and approximate thicknesses of oxide films formed on nitrided steel. (See reference 8.)

The characteristic colors of various portions of the piston-ring cross section and their corresponding ratings are listed in table II. The specimen was heated until the core was red purple and the case was dark blue when examined without magnification.

When examined at 1500 diameters with the light microscope, the region near the running face in the cross section of the ring exhibited marked differences in color, which indicated varying degrees of oxidation. The smooth portion of the coating was yellow orange. This thin oxide film corroborated earlier statements as to the corrosion resistance of the coating (reference 1). The granular coating, however, possessed a much thicker oxide film, the colors of which suggested that the oxidation rate of this area was nearly that of the case. Between this coating layer and the worked crystals was a thin deep-orange band of coating whose oxidation rate was less than that of either the rough coating or the worked crystals.

Figure 10 is the area shown in figure 9 after the specimen had been heat-tinted. The broad dark band below the yellow-orange oxide film of the smooth coating consisted of blue and purple granules. The orange line lying between this band and the worked crystals did not register on the monochromatic film.

The worked layer lying just under the coating was light blue, which indicated an oxidation rate slightly greater than that of the nitrided case. The lower ends of the bent surface crystals located deeper in the case tinted gradually to the intermixed deep-orange and blue needle-shaped crystals characteristic of the case. The color changed rather abruptly from the case hues to the intense red-orange and yellow-orange crystals of the core. The core was apparently more resistant to oxidation than the case. The colors of the crystals resembled the tint of the smooth portion of the coating. The "white nitrides" were brown, which suggested a surface activity lying between that of the case and the core.

## Electron Micrographs of Piston-Ring Cross Sections

When only a small deformation of the crystals under the running face of the ring occurred, the surface crystals exhibited few signs of severe working, the only indications of deformation being the slight bending of the crystals at the surface. In an area where severe working was evident (fig. 11), the crystals were bent almost parallel to the surface. This specimen was etched in nital and the increased attack on the strained and fragmented crystal plates made

the crystals appear to have been ground up. If any coating had formed on the surface, it lay between the vaguely defined line of the ring surface and the deformed crystals. These crystals probably correspond to the worked crystals under the coating in figure 9.

An electron micrograph of a coating area similar to figure 9 is shown in figure 12. Only the top smooth portion of the coating and part of the granular area are visible in the print. The original negative showed the lower edge of the coating as an abrupt line of demarcation to an area resembling figure 11. The smooth portion of the coating showed no definite structure even when electron micrographs were taken at the highest magnification of the electron microscope and enlarged optically to 100,000 diameters.

The granular area below the smooth coating seemed to be composed of small fragments whose structure was finer and more randomly oriented than that of the severely worked and stratified layers lying underneath the coating proper. The granular structure diffused gradually into the smooth layer with no sharp line of demarcation.

The area lying in the plane of the photograph just below the severely worked crystals of an area similar to figure 11 is shown in figure 13. The center of the area shown in figure 13 occurred about 0.0007 inch below the ring surface. The ridges of unetched material characteristic of the nitrided area appeared as smooth irregular bands with the finely pitted areas of the strained crystals etched to a lower level. The unetched ridges usually have lamellar sides. Figure 14 is an electron micrograph of the nitrided case below the worked area. The lamellar-sided ridges were still present but the crystal faces did not etch into the fine pits shown in figure 13.

## Electron Micrographs of the Piston-Ring Running Face

The running faces of unetched new and used rings were examined for evidence of pitting or corrosion. Both new- and used-ring surfaces were free of pits and etched areas. The new ring was smooth except for parallel shallow grooves imparted by the finishing operation. The used ring resembled the new ring with a less prominent series of grooves and an occasional slight welt such as might be caused by metal flow.

When etched with nital, the used-ring surface was revealed to consist of broad plateaus that remained unattacked and smaller

unetched plateaus, which were apparently the tops of crystals bent over parallel to the surface. Figure 15 is an electron micrograph of a nominally uncoated area as seen in cross section in figure 11. The crystal tops were bent over and were covered with a thin film of amorphous material. Some evidence of slipband formation occurred in the smooth portion of the crystals not directly on the surface. The severely worked crystal layers such as appear in figure 11 can be seen under the lips of the bent-over smooth edge.

An actual coating area, which gave a visible cross section such as can be seen in a photomicrograph, often extended beyond the limits of the field available in the electron microscope. Figure 16 shows the edge of such a coating area. The smooth coating occupies the lower half of the figure and the area of strained crystal edges slopes down from the coating plateau to a surface visible at the top of the picture, which resembles the unworked case crystals in figure 14.

The face of the new ring was severely etched by nital, as might be expected from its relatively undistorted surface crystals. Small smooth patches were present, however, which were apparently the same as the coating on the used rings. The size and the appearance of the smooth patches suggested that they were formed in the same manner as the coating on the worn rings with the abrasive grains from the finishing operation generating the heat and pressure as mentioned in reference 9.

The new and the used rings were treated with aqua regia after the nital etch in order to verify the chemical resistance of the coating. The extent of the coating areas decreased but electron micrographs of the remaining coating areas revealed these areas to be substantially unchanged. The new ring was much the same with smooth spots still present although their edges had been rounded as shown in figure 17.

After the aqua regia etch, the new- and used-ring segments were boiled for 30 minutes in concentrated potassium hydroxide. The segments turned dark, which suggests the formation of an oxide coating. Several preliminary Lucite impressions were used to clean the oxide from the surface before the final replicas were made. The general surface of the new ring presented two markedly different types of etching. In areas where surface working had apparently occurred, the smooth spots remain unattacked. The worked crystal face adjacent to the spots was etched to form a columnar structure much different from the lacework type of etch observed

after using nital. This difference can be seen by comparing figures 15 and 18. Unworked surface areas, on the other hand, were severely attacked but no preferential etching was apparent. The uniform pebble-grained etch characteristic of this type of area is shown in figure 19.

The potassium hydroxide etch had no marked effect on the coated areas of the used piston ring other than to round off slightly the sharp edges imparted to the crystals by the nital etch. The uncoated areas of the used ring still resembled figure 15 but the bent crystal tops were undermined at the edges, giving the effect of a pile of irregular crystals plates.

## DISCUSSION

### Crystal Fragmentation and Formation of Microcrystals

Extensive work has been conducted on the severe distortion of metals and the accompanying crystallographic changes. Wood (reference 10) found that metal crystallites could be ground only to a limiting size of approximately $10^{-5}$ centimeters. Bridgman (reference 11) obtained similar results in extreme pressure distortion of metals. Harker (reference 12) found that severely deformed metals recrystallized into small crystallites immediately after deformation. With the exception of work in electron and X-ray diffraction, the recent utilization of the electron microscope for surface studies has tended to show the presence of surface films, which are either amorphous or so finely crystalline that the crystallites are beyond the resolving power of the replica methods currently used (reference 13). This estimate of crystal size agrees with the work of Bridgman (reference 11), who found that in some cases the extreme pressure smearing of a metal generated a material of such fine structure that an estimate of the residual grain size by X-ray diffraction gave a value of 10 A.

The controversy as to whether amorphous layers of metals are formed during polishing has not been settled. Much of the difference of opinion has been in the interpretation of diffuse ring patterns resulting from electron diffraction. Some investigators believe that a polished surface consists of a thin amorphous film under which lie oriented microcrystals (reference 14). Others believe that diffuse surface patterns can come from crystalline material having no surface projections suitable for diffraction (reference 15).

## Piston-Ring Coating

The physical distortion of the surface crystals was striking evidence of the sliding pressures present on the piston-ring face. The most severe distortion occurred when the ring face was jammed against the cylinder barrel just after engine ignition. The grooves worn in the cylinder barrel and the slow rotation of the piston ring during engine operation would allow a piston ring to ride on the barrel projections. The small contact area with the resulting high surface loading would cause localized extreme pressure and extreme temperature effects.

X-ray studies of wear products have revealed the wear process to be a rapid heat treatment of the test surface accompanied by rapid fluctuations of temperature (reference 16). This process is borne out by electron-diffraction studies of machine-ground surfaces (reference 9).

Flash temperatures resulting from frictional heating of surfaces decrease rapidly with depth of heat penetration. In grinding operations the surface can be melted and only an annealing effect will occur $10^{-4}$ centimeters below the surface (reference 9). This depth of heat penetration and the accompanying structure changes are similar among specimens if the same metals are used. Thus with a given metal combination where the physical conditions are in a given range, the type of surface distortion with depth should be consistent. The thickness of the smooth coating varied through a small range relatively independent of the degree of working of the underlying surface as can be seen in figures 7 and 9. This lack of thickness variation suggested that the heat-conduction differential for nitrided steel under the conditions of ring-friction temperatures found in normal engine operation allowed the ring face to melt to a limiting depth of approximately 0.0001 inch. Thinner smooth layers than those present in figures 7 and 9 were observed but a thicker layer was seldom present except at the edge of the ring.

The formation of a smooth coating without accompanying severe underlying surface distortion suggested that the formation of this type of layer is due primarily to a friction-temperature effect whereas the formation of the rough coating is due primarily to a pressure-smearing effect. The low pressure friction of the barrel ridges on the rapidly moving ring could melt the surface crystals without seriously distorting the surface, as shown in figure 7. The gradual change from the rough to the smooth phases shown in figure 12 supported this view. The surface of the rough coating

was apparently heated to a temperature sufficient to melt the smeared microcrystals to a depth of 0.0001 inch. The formation of two phases may have been simultaneous. The dynamic quality of the surface alteration would allow the coating formation to occur in a number of combinations, as can be judged from a comparison of figures 7, 8, and 9.

## Mechanism of Coating Formation

Electron-micrograph studies of the running face and the cross sections of nitrided-steel piston rings revealed several features of the coating-formation process that heretofore had been only indirectly studied by electron and X-ray diffraction methods. This information when coupled with the results of the oxidation heat-tinting and the work of other investigators as listed in the references indicated that the coating may have been formed in the following manner: The nitrided-case crystals first bent along their planes of easy slip (reference 17(a)) until the distorted crystal layers were almost parallel to the surface (reference 10) as shown in figures 8, 9, and 11. This action work-hardened and strained the crystal plates until they developed virtual microcrystals within the strained layers as indicated in figures 11 and 13 (references 17(a) and 18(a)). Increased pressure and temperature weakened the strain junctions of the virtual crystallites (reference 18(b)) until the plates detached themselves from the surface and fragmented, smearing over the worked layers whose depth below the surface or whose position in front of the pressure point had allowed them to remain a part of the coherent worked layer shown in figure 8. This process may have repeated itself in the same area to give a lamellar effect as shown in figure 8.

The increased temperature that resulted from the internal and external friction forces acting on the crystals (reference 17(b)) tended to oppose the work-hardening. This heat annealed the hardened microcrystals as suggested in figure 10. The increased temperature also caused a local melting and recooling, which had the effect of sintering the ground-up microcrystals and welding them to the worked crystal layers.

The friction between the top of the granular smear and the barrel generated a flash temperature sufficient to melt the smear to a depth of approximately 0.0001 inch (reference 9) as shown in figures 7, 9, and 12. When the pressure-friction wave had passed, the film solidified in an instant before crystals of any appreciable

size had a chance to develop (reference 11) as shown in figure 12. This process was continuous, the coating being formed and reworked in all possible combinations of the preceeding outline.

## Oxidation Rate as Indication of Strain

The difference in oxidation rate of various portions of the ring cross-sectional area seemed to be dependent not only on the crystal-plane orientation but also on the degree of strain of the crystals. Strained crystals possessed more internal energy than unstrained crystals (reference 18(c) and (d)) and, as indicated in a comparison of figures 13 and 14, strained crystal surfaces tended to etch to a greater extent than unstrained crystals. X-ray studies of nitrided steel have shown that the nitriding process strains the crystals wherever the nitrides are formed at the crystal boundaries (reference 19). Where the iron is almost completely changed to iron nitride, however, the degree of strain is less.

An examination of the oxide-film colors on the used piston ring revealed the thickness of the coating of the core, case, and white nitrides to be in the order of strain; the greater the strain of the crystal, the thicker the oxide film. This variation in thickness was consistent with the idea of a strained crystal having a greater available surface energy than an unstrained crystal. On the basis that the thickness of the oxide film is proportional to the strained condition of the crystals, not only the general degree of strain of a crystal area can be determined but also the points of discontinuity of strain. The color-tinted ring cross section can therefore be analyzed as follows: The unnitrided central portion of the ring had the thinnest oxide coating of the cross section, which indicated a relatively unstrained alloy. The blue and orange crystals of the case indicated a greater degree of strain than was present in the core, as a result of the nitriding process. The bent and worked crystals of the case near the surface were strained even more than the case because of the working and deformation.

The abrupt demarcation to the orange transition line pointed out the line of rupture of the original surface. This orange film, which indicated reduced strain, may mean that this portion of the ring was similar in structure to the smooth coating. The extra heat of friction that resulted from rubbing the ground-up microcrystals over the freshly cleft surface could have caused a melting, which would have welded the sintered crystal smear to the newly exposed surface.

The broad dark line of the blue and purple crystallites seen in figure 10 consisted of particles of the same general oxidation rate as the undeformed case. This similarity in color suggested that the granular portion of the coating still consisted of microcrystals of nitrided steel, which had been stress-relieved by the annealing action of formation.

The yellow-orange film of the smooth coating indicated a marked difference in oxidation rate between the smooth and rough portions of the coating. The smooth coating may have consisted of extremely small microcrystals too small to be resolved in the electron microscope, which recrystallized from the melted surface when it solidified (reference 11). If this recrystallization had occurred, the possibility of the denitriding of the smooth coating by the flash melting of the surface layer should be considered, inasmuch as the color of the smooth coating film was approximately that of the unnitrided core of the ring. The thickness of oxide films should not be considered proof of the above statement, however, inasmuch as the melted surface coating may have formed a vitreous layer on cooling that was less open to surface oxidation than the granular portion of the coating (reference 9).

## Structure of Piston-Ring Coating

The experimentation that served as a basis for this report revealed the coating structure to be more complex than was originally supposed. Figures 7, 8, and 9 have shown that the coating consisted of both smooth and granular layers. Figures 12, 15, and 16 show a smooth structure that contained little evidence of crystallinity. A coating area similar to figure 16, when enlarged to 100,000 diameters, still revealed no evidence of structure other than a vague nodulation that might have been characteristic of the silica film at this magnification.

The silica replica has an average resolution of 50 A, which is one-twentieth of the minimum crystal size found by Wood in his metal deformation experiments (reference 10). The granular structure of the coating shown in figure 12 was, however, within the limits specified by Wood, the nodular particles being approximately $10^{-5}$ centimeters across. As can be seen in figures 12, 15, and 16, the smooth coating had a much finer structure than this $10^{-5}$-centimeter limiting size.

The formation of smear spots on both the new and the used rings and the similar results obtained with the etching reagents seemed to indicate that both types of smear were the same. It is improbable that a structure existed in the smooth coating that was not resolved because of its resistance to chemical attack, inasmuch as the coating oxidized to the same extent as the ring core, and the coating areas decreased with subsequent etches. The aqua regia and the potassium hydroxide should have etched through a metallographic polish layer 20 to 30 A thick and should have revealed any slight granularity indicative of the 100 A microcrystals predicted by Lees (reference 14). A film of this dimension would account for only the top 0.1 percent of the total smooth coating thickness shown in figure 12. The lack of apparent structure must be due therefore not to a resistant material that cannot be etched but to a sluggishly reacting layer of smooth smeared metal, which is either virtually amorphous or of exceedingly small crystal size. In either case, the determination of residual crystallinity is difficult if not impossible inasmuch as crystals of this size give diffuse rings, which cannot always be distinguished from the diffuse rings generated by a liquid surface, when studied by electron or X-ray diffraction. If recrystallization of the smooth coating occurred, the resulting particles were smaller than the limit of resolution of the electron microscope. Bridgman's work with extreme crystal distortion (reference 11) revealed the presence of extremely small crystals or crystalline residues that, on the basis of the line broadening of the X-ray rings, seemed to be on the order of 10 A across.

## Composition of Coating

The coating material seemed to come mainly from the piston rings themselves. The piston-ring face was in constant contact with the hot friction wave; whereas the barrel-surface increments had only momentary contact and could dissipate the heat much more readily than the piston ring with less resulting surface destruction. The appearance of tongues of distorted crystals projecting into the smooth coating tended to verify the formation of the coating from the ring material.

The composition of the granular portion of the coating was probably similar to that of the case. Work described in reference 2 indicated that a residue of austenitic structure may remain from the incomplete transformation to ferrite after the temperature effects incurred during the smear formation. The smooth coating may have contained crystal fragments of both types of structure along with

traces of oxides (references 2, 9, and 16) but the bulk of the material was probably the same as the granular layer, although it may have been denitrided. If the smooth coating were nickel, chromium, or an oxide, it would not form an oxide film at the tinting temperatures used. Spectrographic analysis has shown that the faces of the new and used rings give the same spectra (reference 1). This result ruled out the formation of the coating by foreign metal or alloys.

## CONCLUSIONS

These conclusions are based on a study by means of the light microscope and the electron microscope of nitrided-steel piston rings run in nitrided-steel cylinder barrels and on the analysis of the work of other investigators as listed in the references. The statements made apply specifically to nitrided-steel piston rings run in nitrided-steel cylinder barrels but much of the information is generally applicable to the mechanisms of wear and surface deformation of rubbing metals.

Conclusions 1 to 5 are final interpretations of the light micrographs and electron micrographs taken of the nitrided-steel piston rings. The statements in conclusion 6 regarding the mechanism of the coating formation are not intended as a theory in its final form but as an explanation of the phenomena observed. In each step the most logical of several possible mechanisms has been chosen. At the present time all other possibilities for each step of the mechansim discussed cannot be absolutely eliminated and the conclusions are drawn with this inherent limitation in mind:

1. The running faces of nitrided-steel piston rings smeared during engine operation and an adherent layer consisting largely of piston-ring material was formed on the running face.

2. The adherent coating layer usually consisted of a virtually amorphous crust with an underlayer of finely fragmented crystals.

(a) The granular portion of the coating was made up of crystallites of nitrided-steel that had been fragmented to a limiting size and then welded to the underlying surface.

(b) The smooth portion of the coating was the result of the flash melting and the rapid solidification of either the granular coating or of worked surface layers.

3. The smooth portion of the coating had a vitreous-appearing structure that was virtually amorphous. No discernible structure was visible in the replicas of the coating material at the limit of resolution of the electron microscope. Any crystals or crystal fragments present in this layer were less than 100 A across.

4. The granular portion of the coating layer consisted mainly of small particles approximately 1000 A across, which appeared to be pressed and sintered together.

5. The granular portion of the coating layer had chemical properties similar to those of the underlying nitrided steel. The smooth top layer had a greater resistance to oxidation and corrosion than did the granular portion of the coating and the nitrided steel.

6. The coating layer found on nitrided-steel piston rings that had been run in nitrided-steel cylinder barrels was formed in the following manner:

(a) High pressures traveling along the surface bent the surface crystals parallel to the running face.

(b) The strains induced caused the crystals to separate along their slip planes and the lamellae slid over each other.

(c) The slip-plane lamellae developed virtual microcrystals within themselves as a result of severe work-hardening.

(d) Increased pressure and elevated temperatures weakened the slip-plane intersections until the lamellae separated from the worked surface and fragmented, the crystallites grinding to a limiting size dependent upon the metallurgical characteristics of the alloy.

(e) The increased heat engendered during this process partly melted and annealed the crystal fragments, sintering them into a coherent film to form the granular layer.

(f) The increased boundary friction between the smearing crystals and the intact worked slip planes generated a thin molten layer of metal, which welded the sintered film to the underlying worked layers as it cooled.

(g) The formation of the smooth portion of the coating may have occurred with the same or subsequent strokes to the one which produced the granular smeared layer.

(h) The friction between the top of the granular smear of crystals and the barrel generated a flash temperature sufficient to melt the smear to a depth of approximately 0.0001 inch.

(i) When the pressure point had been passed, the film solidified in an instant, freezing the crystal pattern before crystals of any appreciable size had a chance to develop.

(j) The process was continuous, the coating having been formed and reworked in all possible combinations of the preceeding outline.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, November 13, 1945.

## REFERENCES

1. Bobrowsky, A. R., Kittel, J. Howard, and Boegli, Charles P.: Experimental Study of the Coating Formed on Nitrided-Steel Piston Rings during Operation in Nitrided-Steel Cylinders. NACA ACR No. 4C31, 1944.

2. Good, J. N., and Brockway, L. O.: An Electron and X-ray Diffraction Investigation of Surface Changes on Nitrided-Steel Piston Rings during Engine Operation in Nitrided-Steel Cylinder Barrels. NACA ACR No. E4L27, 1945.

3. Kittel, J. Howard, and Vierthaler, Walter A.: Experimental Study of the Coating Found on Scuffed Cast-Iron Piston Rings during Operation in Nitrided-Steel Cylinders. NACA ACR No. E4K02, 1944.

4. Burton, Charles J., Barnes, R. Bowling, and Rochow, T. G.: The Electron Microscope. Calibration and Use at Low Magnifications. Ind. and Eng. Chem., vol. 34, no. 12, Dec. 1942, pp. 1429-1436.

5. Heidenreich, Robert D.: Interpretation of Electron Micrographs of Silica Surface Replicas. Jour. Appl. Phys., vol. 14, no. 7, July 1943, pp. 312-320.

6. Heidenreich, R. D., and Peck, V. G.: Fine Structure of Metallic Surfaces with the Electron Microscope. Jour. Appl. Phys., vol. 14, no. 1, Jan. 1943, pp. 23-29.

7. Powell, Allen S., Clark, Thomas P., and Shaw, Milton C.: Investigation of a Method of Comparison of Metallic Surface Contours by Means of Stereoscopic Electron Micrographs. NACA ARR No. E5A05a, 1945.

8. Chalmers, Bruce: The Physical Examination of Metals. Vol. I. Optical Methods. Edward Arnold & Co. (London), 1939, pp. 76-97.

9. Wulff, John: The Metallurgy of Surface Finish. Proc. Special Summer Conf. on Friction and Surface Finish at M.I.T. (Cambridge, Mass.), June 5-7, 1940, pub. by Chrysler Corp., 1940, pp. 13-21.

10. Wood, W. A.: Structure of Metals under Deformation. Nature, vol. 143, no. 3613, Jan. 28, 1939, pp. 163-164.

11. Bridgman, P. W.: Flow Phenomena in Heavily Stressed Metals. Jour. Appl. Phys., vol. 8, no. 5, May 1937, pp. 328-336.

12. Harker, David: On the Structure of a Metal During Deformation. Jour. Chem. Phys., vol. 10, no. 11, Nov. 1942, p. 692.

13. Heidenreich, Robert D.: Techniques in Applied Electron Microscopy. Jour. Opt. Soc. Am., vol. 35, no. 2, Feb. 1945, pp. 139-148.

14. Lees, C. S.: The Structure of Polished Metal Surfaces. Trans. Faraday Soc. (London), vol. XXXI, 1935, pp. 1102-1105; discussion, pp. 1105-1106.

15. Burwell, J. T.: Diffuse Electron Diffraction Patterns. Jour. Chem. Phys., vol. 6, no. 12, Dec. 1938, pp. 749-751.

16. Goldschmidt, H. J., and Harris, G. T.: An X-ray Examination of Mechanical Wear Products. Jour. Sci. Instr. (London), vol. 18, no. 5, May 1941, pp. 94-97.

17(a). Barrett, Charles S.: Slip in Metal Crystals. Structure of Metals, ch. XV, McGraw-Hill Book Co., Inc., 1943, pp. 288-307.

(b) Barrett, Charles S.: The Theory of Dislocations. Internal Friction. Structure of Metals, ch. XVI, pp. 341-344.

18(a). Seitz, Frederick: The Slip Process. The Physics of Metals, ch. VI, sec. 18, McGraw-Hill Book Co., Inc., 1943, pp. 73-78.

(b). Seitz, Frederick: Grain-boundary Influence. The Physics of Metals, ch. VII, sec. 25, pp. 107-113.

(c). Seitz, Frederick: The Change in Energy and the Distortion Accompanying Cold-work. The Physics of Metals, ch. VI, sec. 19, pp. 78-81.

(d) Seitz, Frederick: Hypothetical Mechanism of the Slip Process. The Physics of Metals, ch. VI, sec. 22, pp. 85-101.

19. Betteridge, W.: The Structure of the Nitride Case on an Austenitic Steel. Jour. Sci. Instr. (London), vol. 22, no. 2, Feb. 1945, pp. 28-29.

TABLE I - VISUAL HEAT-TINTING OF NITRIDED-STEEL PISTON RINGS

[Film thickness values given in this table, which are approximate, are taken from reference 8.]

| Case | | Core | |
|---|---|---|---|
| Color | Film thickness (A) | Color | Film thickness (A) |
| Light tan | | Clear | |
| Tan | 460 | Light tan | |
| Brown | | Tan | 460 |
| Brown purple | 520 | Yellow orange | |
| Red purple | | Orange | |
| Purple | 630 | Red orange | |
| Dark purple | 680 | Brown purple | 520 |
| Dark blue | 720 | Red purple | |
| Light blue | | Dark purple | 680 |
| Light blue | | Dark blue | |
| Greenish blue | | Light blue | |

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TABLE II - OXIDE-FILM COLORS OF MICROSTRUCTURAL COMPONENTS OF CROSS SECTIONS OF USED NITRIDED-STEEL PISTON RINGS

[The piston-ring segment was heated to approximately 300° C on a brass block with an electric hot plate. The comparative oxidation numbers signify the extent of the oxidation of the components; the larger the number, the greater the rate of oxidation.]

| Components | Comparative oxidation | Color |
|---|---|---|
| Coating - smooth top layer | 1 | Yellow orange |
| Coating - rough middle layer | 5 | Mixed blue and purple granules |
| Coating - rough layer at intersection of worked layer | 3 | Deep orange |
| Worked layer under coating | 6 | Intense light blue |
| Bent crystals under worked layer | 5 | Intermixed deep-orange and light-blue crystals |
| General case appearance | 5 | Intermixed deep-orange and light-blue crystals |
| General core appearance | 2 | Intermixed red-orange and yellow-orange crystals - light-blue network between crystals |
| White nitrides | 4 | Brown |

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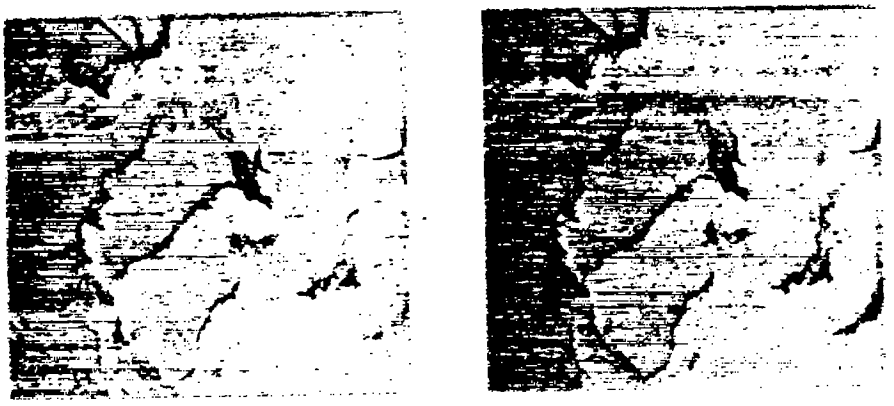

Figure 1. - Electron stereomicrograph of running face of used nitrided-steel piston ring showing bent-over crystals and worked-crystal layers. Etched in nital. X6000.

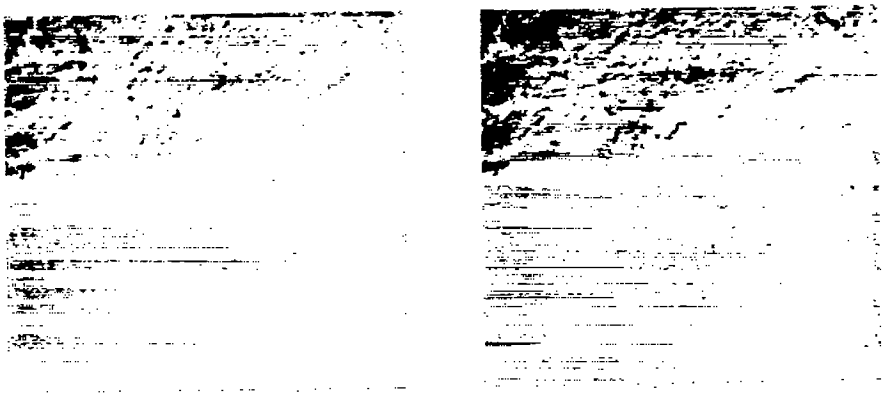


Figure 2. - Electron stereomicrograph of running face of used nitrided-steel piston ring showing coating area and worked-crystal layer. Etched in nital. X6000.

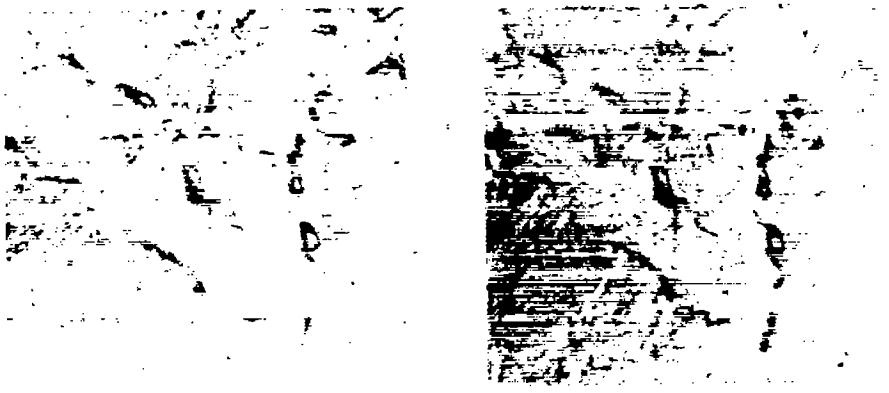

Figure 3. - Electron stereomicrograph of cross section of used nitrided-steel piston ring showing strained crystals and nitrided ridges just under surface of ring. Etched in nital. X6000.

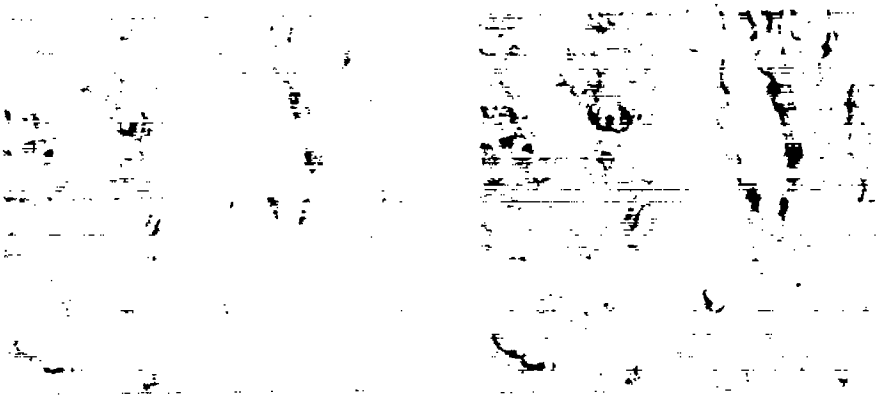


Figure 4. - Electron stereomicrograph of cross section of used nitrided-steel piston ring showing nitrided case below worked-crystal area. Etched in nital. X6000.

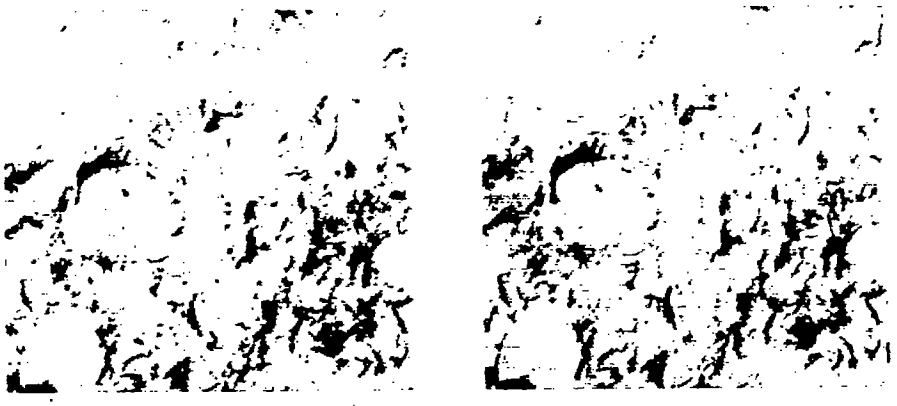

Figure 5. - Electron stereomicrograph of running face of new nitrided-steel piston ring showing worked surface. Etched in potassium hydroxide. X6000.

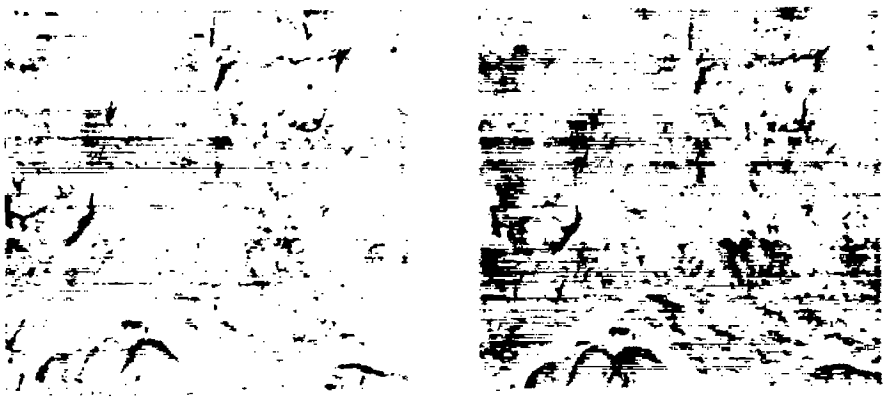


Figure 6. - Electron stereomicrograph of running face of new nitrided-steel piston ring showing unworked surface. Etched in potassium hydroxide. X6000.

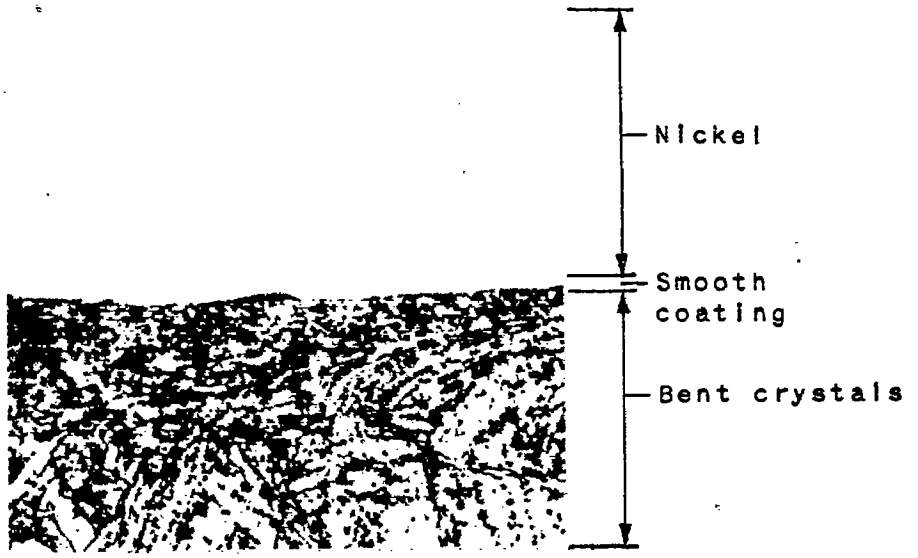


Figure 7. - Light micrograph of cross section of used nitrided-steel piston ring showing smooth coating. Etched in nital. X1500.

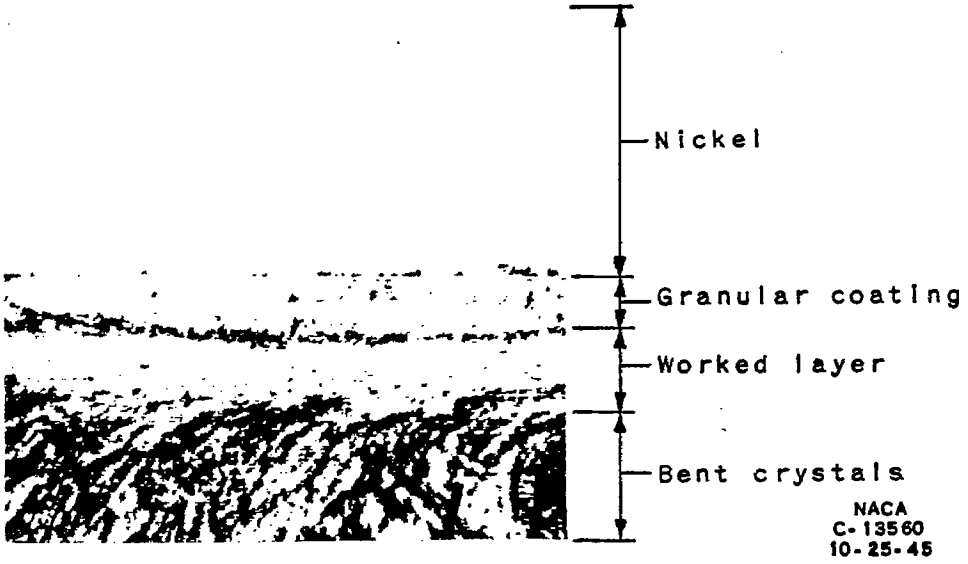


Figure 8. - Light micrograph of cross section of used nitrided-steel piston ring showing granular coating. Etched in nital. X1500.

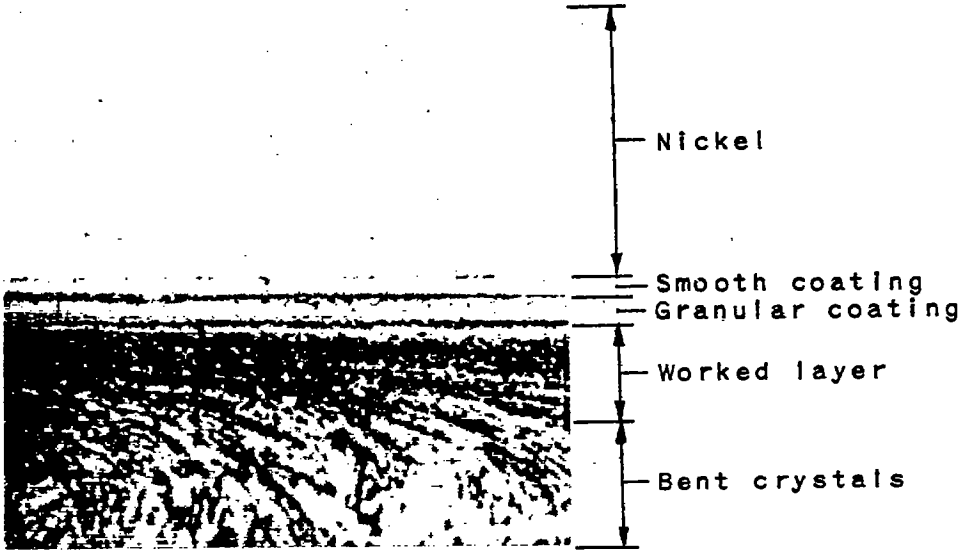


Figure 9. - Light micrograph of cross section of used nitrided-steel piston ring showing both smooth and granular coating. Etched in nital. X1500.

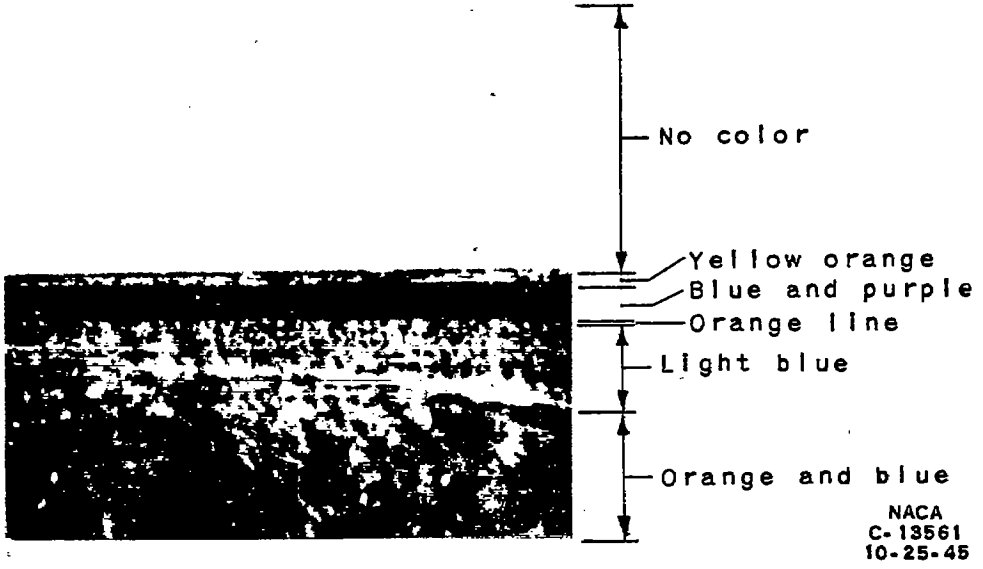


Figure 10. - Light micrograph of cross section of used nitrided-steel piston ring shown in figure 9. Etched in nital and heat tinted at 300° C. X1500.

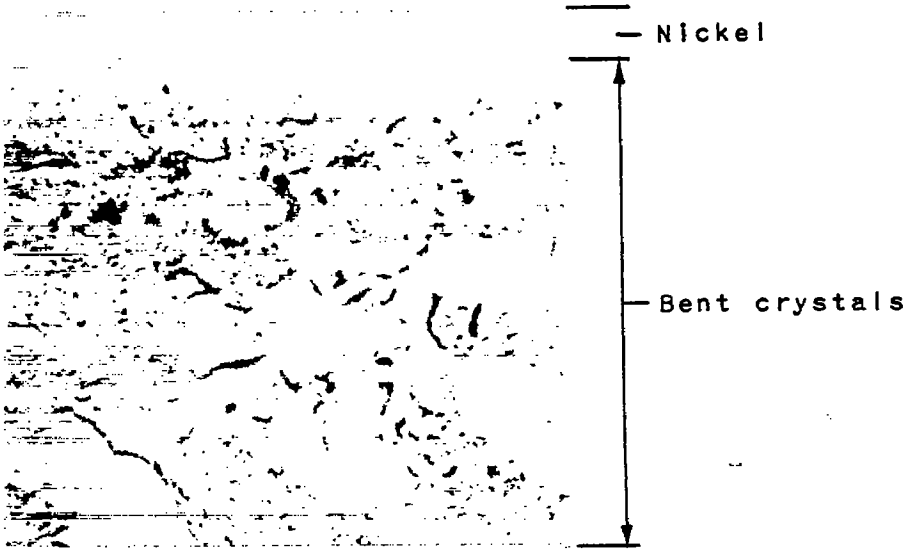


Figure 11. - Electron micrograph of cross section of used nitrided-steel piston ring showing bent and severely worked crystals. Etched in nital. X10,000.

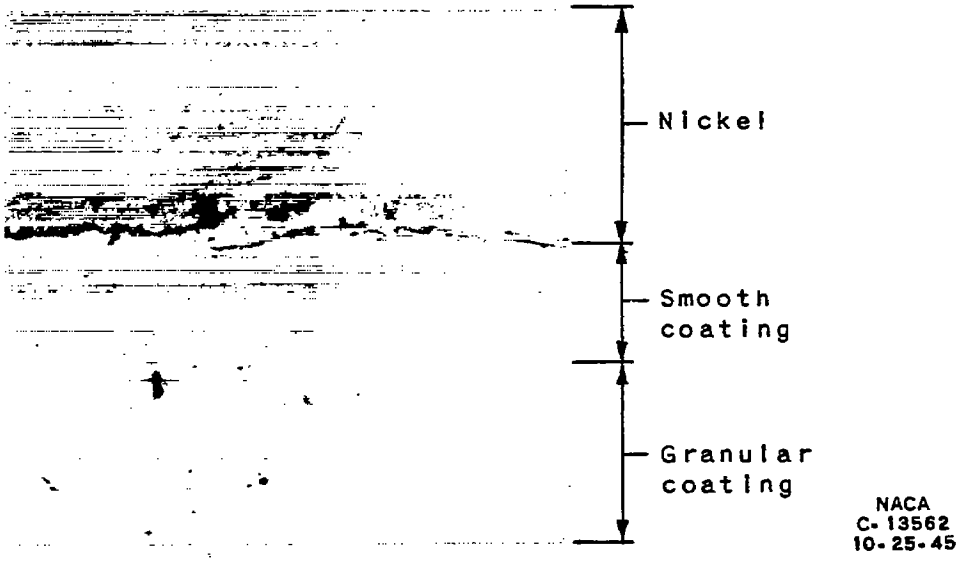


Figure 12. - Electron micrograph of cross section of used nitrided-steel piston ring showing smooth and granular coating. Etched in nital. X10,000.

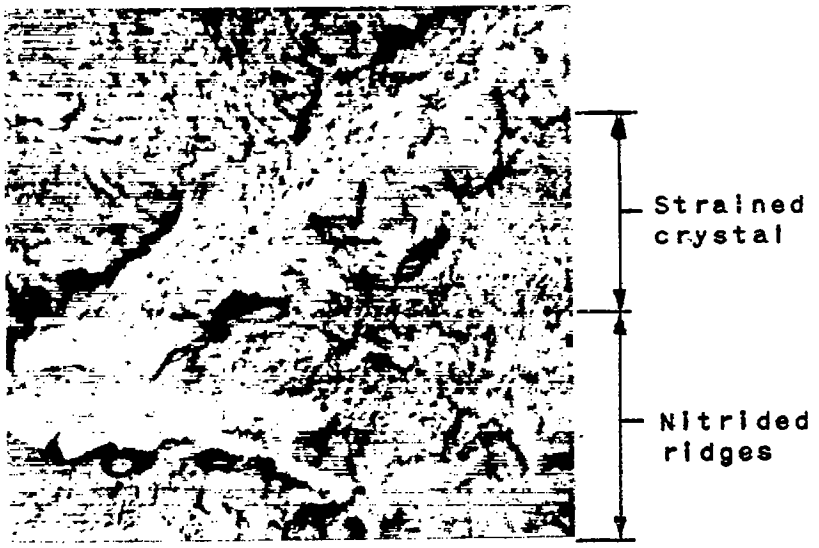


Figure 13. - Electron micrograph of cross section of used nitrided-steel piston ring showing strained crystals and nitrided ridges just under surface of ring. Etched in nital. X10,000.

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Figure 14. - Electron micrograph of cross section of used nitrided-steel piston ring showing nitrided case below worked-crystal area. Etched in nital. X10,000.

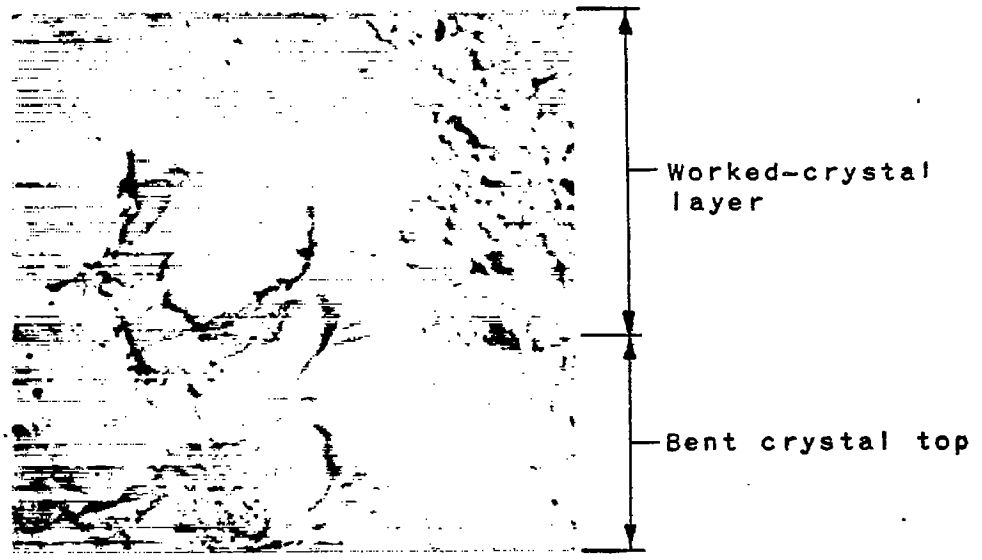


Figure 15. - Electron micrograph of running face of used nitrided-steel piston ring showing nominally uncoated area with bent-over smeared crystals and worked-crystal layer. Etched in nital. X10,000.

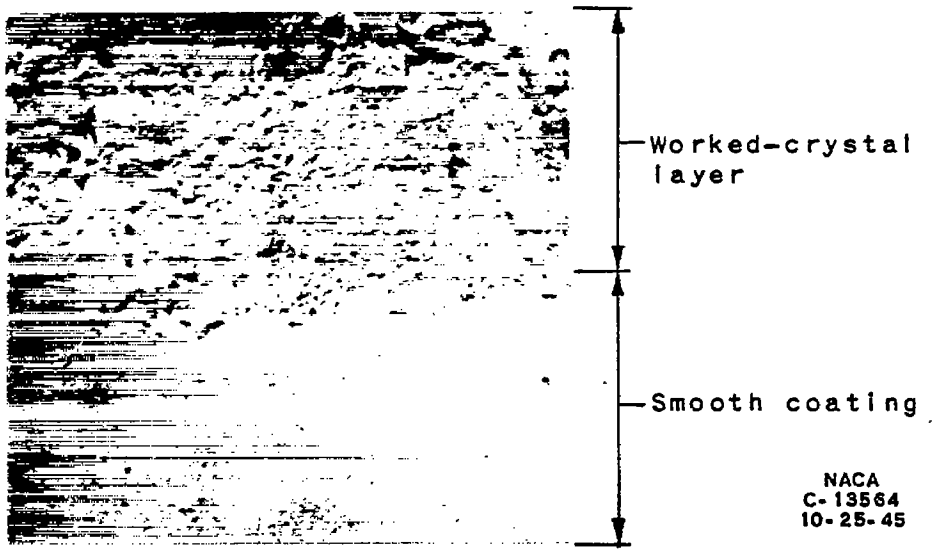


Figure 16. - Electron micrograph of running face of used nitrided-steel piston ring showing coating area and worked-crystal layer. Etched in nital. X10,000.

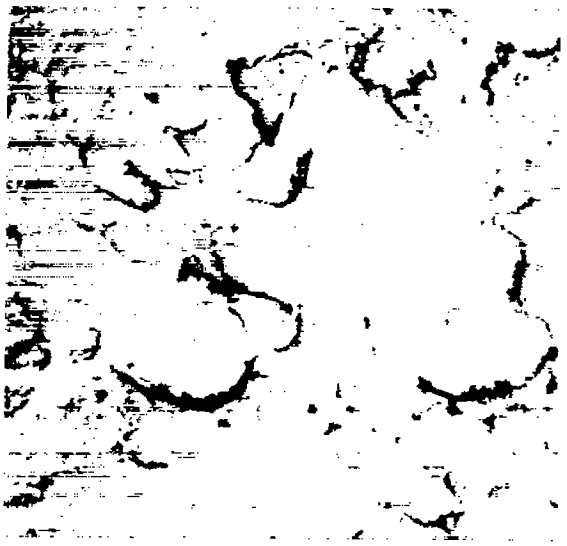

Figure 17. - Electron micrograph of running face of new nitrided-steel piston ring showing smears probably caused by abrasive particles. Etched in nital and aqua regia. X10,000.

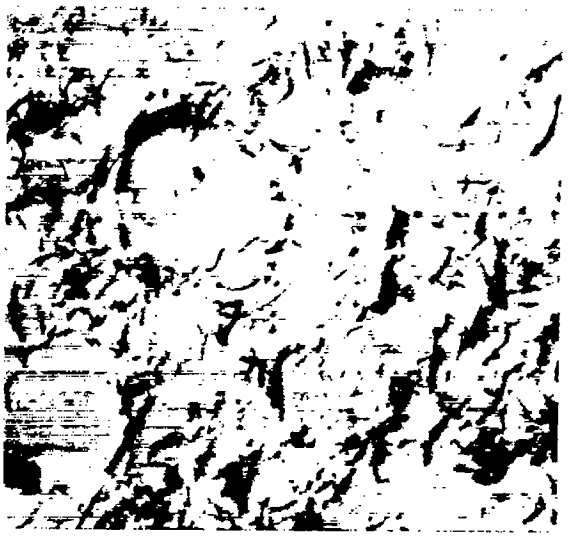

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Figure 18. - Electron micrograph of running face of new nitrided-steel piston ring showing worked surface area. Etched in potassium hydroxide. X10,000.

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Figure 19. - Electron micrograph of running face of new nitrided-ring showing unworked surface area. Etched in potassium hydroxide. X10,000